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[2]Rotaxane with a cation-binding wheel

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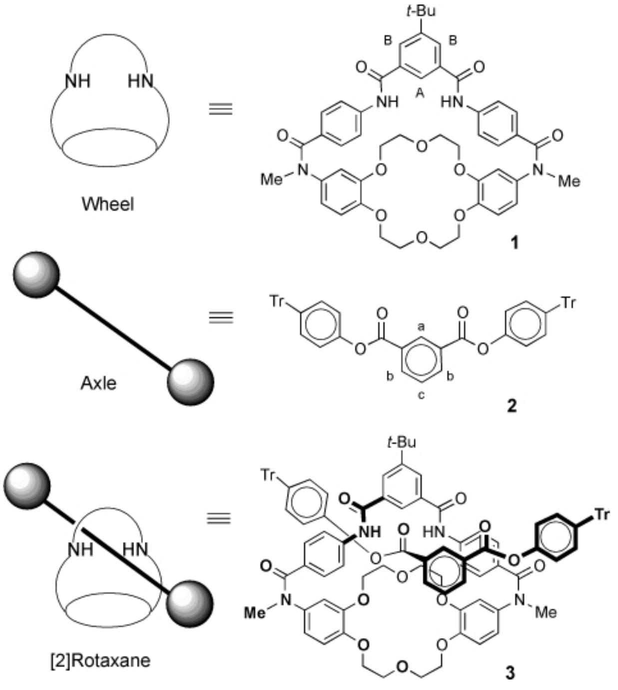
A [2]rotaxane with a crown ether-containing wheel component is synthesized and shown to bind K^+ which alters the rotaxane's dynamic properties.

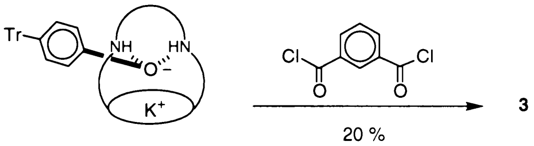
There is a growing interest in the chemistry of mechanically interlocked molecules.[1–6] This report concerns rotaxanes, interlocked molecules that are comprised of two molecular components, a wheel and a penetrating axle. Rotaxanes can exhibit a number of dynamic features such as shuttling (the wheel sliding along the axle),[1] pirouetting (the wheel rotating around the axle),[7] and unthreading (loss of the axle from the wheel).[8] There is hope that these dynamic features can be controlled and eventually utilized in molecular machines.[9,10] At present, a major research goal is to develop switching strategies to regulate these dynamic features.

Most of the rotaxanes reported to date have used macrocyclic wheels.[1] We are interested in macrobicyclic wheels with the generalized structure shown in Scheme 1. The structure is composed of a cation-binding macrocycle (*e.g.*, crown ether, porphyrin, *etc*.) and an anion-binding bridge [*e.g.*, diamine, bis(amide), *etc*.]. The anion-binding bridge should allow a range of rotaxanes to be prepared using the versatile anion-templated methodology recently introduced by Vögtle and coworkers.[11,12] The wheel component in these rotaxanes can bind metal cations which in turn should influence the rotaxane's dynamic processes.

In this initial study, we use the bridged crown ether **1** as the rotaxane's wheel component. Recently, we reported a six-step, gram-scale synthesis of **1** and demonstrated that a close structural analogue can simultaneously bind an alkali metal cation and a halide anion.[13] Based on this knowledge, we reasoned that host **1** should be able to bind the potassium salt of 4-tritylphenolate, and that the resulting 'wheeled potassium phenolate' **4** would react with isophthaloyl dichloride to form [2]rotaxane **3**. Indeed, we can consistently produce **3** in 20% isolated yield.† The compound is thermally stable, for example, heating a DMSO solution at 413 K for 3 h produces no evidence of rotaxane unthreading.



Scheme 1



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The structure of **3** was proved by NMR and mass spectrometry. A positive ion FAB mass spectrum shows a weak molecular ion signal at *m*/*z* 1646 (M+H), and intense signals at 1668 (M+Na) and 1684 (M+K). A sample treated with KCl shows only the signal at 1684 (M+K). The ^1H NMR spectrum is particularly revealing. The signal for the two isophthalate protons, H_b, in axle **2** is a doublet at 8.43 ppm when the axle is free in $CDCl_3$ solution [Fig. 1(a)], but when the axle is part of rotaxane **3** the two protons are no longer chemically equivalent and two doublets at 8.64 and 8.55 ppm are observed (Fig. 1(b)]. The room-temperature ^1H NMR spectrum of **3** in $CDCl_3$ was assigned by a combination of COSY and ROESY methods. Formation of the rotaxane shifts the signals for the wheel's internal bridgehead proton H_A and its two NH residues strongly upfield. Conversely, the axle's central phthalate protons, H_b and H_c, are shifted downfield. The ROESY spectrum indicates that the rotaxane adopts a predominant supramolecular co-conformation in $CDCl_3$ with the wheel and axle oriented as shown in structure **3**. For example, the axle proton H_a interacts

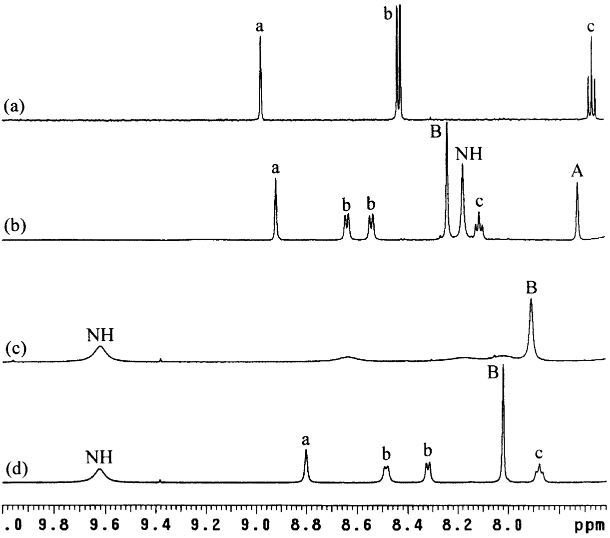

Fig. 1 Partial ^1H NMR spectra (600 MHz, 295 K) of (a) axle **2** in $CDCl_3$, (b) rotaxane **3** in $CDCl_3$, (c) rotaxane **3** in DMSO-d_6 and (d) rotaxane **3** and KPF_6 (5 equiv.) in DMSO-d_6.

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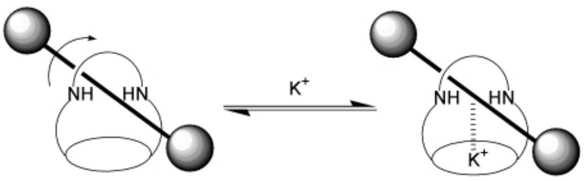
through-space with the wheel NH residues and proton H_A, there are also cross-peaks between axle protons H_b and H_c and the wheel's benzocrown signals.

The ^1H NMR spectrum of **3** in DMSO-d_6 shows broad signals for the axle protons at room temperature [Fig. 1(c)], but they become resolved upon warming. Thus, in DMSO the rotaxane populates multiple axle/wheel orientations.‡ The NMR signals also sharpen upon addition of five mol equivalents of KPF_6 at room temperature [Fig. 1(d)]. There are two possible explanations for this observation: either the added K^+ increases the rate of exchange between different rotaxane co-conformations, or the K^+ freezes out a single co-conformation (Scheme 2).[14] Evidence for the latter explanation is gained from a ROESY spectrum which is consistent with a predominant co-conformation that is different to the one in $CDCl_3$. For example, the axle proton H_a now interacts with the wheel's benzocrown signals whereas the axle proton H_c does not.

Our results suggest that cation-binding macrobicyclic wheels such as **1** can be incorporated into a range of mechanically interlocked structures, and that these compounds are likely to display cation-dependent dynamic behaviour. This is a step towards the eventual development of cation-switchable molecular machines.[9] We gratefully acknowledge financial support from the US National Science Foundation and the University of Notre Dame.



Scheme 2 Binding of K^+ freezes out a single rotaxane co-conformation.

Notes and references

† The anion-templated esterification reactions reported by Vögtle and coworkers require non-polar solvents and a small amount of crown ether to act as a phase-transfer catalyst.[12] In our case, rotaxane formation with salt-binding bicycle **1** is achieved using preformed phenolate salt in a range of organic solvents such as chloroform, THF or even THF–DMF. The reaction fails to yield **3** if the caesium or tetrabutylammonium salt of 4-tritylphenolate is used instead of the potassium salt, which is tentative evidence in favor of **4** as a reactive intermediate.

‡ We have not yet fully characterized the rotaxane's dynamic behaviour. The two most likely motions are pirouetting and shuttling.

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